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THE REACTION OF HIGH POLYMERS IN SOLUTION. THE ALKALINE SAPONIFICATION OF POLYVINYL ACETATE.

Preliminary Report.

By ATSUYASU HORIUCHI.

Introduction.

H. Staudinger¹⁾ reported that when a methanol solution of sodium hydroxide was added to the equivalent quantity of polyvinyl acetate, a white precipitate was produced instantaneously which was left to stand for two hours in a water bath and polyvinyl alcohol was obtained. W. O. Herrmann proposes for this reaction the following equation²⁾:



It is further reported that if potassium hydroxide is used in a quantity less than its equivalent amount, partially saponified products are obtained³⁾, which are distinguished from pure polyvinyl alcohol in being soluble in both water and dioxane and slightly in alcohol.

S. Lee and I. Sakurada⁴⁾ tried to saponify polyvinyl acetate of different polymerisation degrees and monovinyl acetate in methanol water solution with NaOH. By titrating NaOH in the reaction system, the reaction was recognized to be a bimolecular one. Then the velocity constant was calculated and found to have no relation to the polymerisation degree. It was therefore not proper, even from the standpoint of chemical kinetics, to think that the whole ground molecules of polyvinyl acetate at saponification with NaOH were restrained as a huge stiff macromolecule in the shape of a pole. On the contrary, each of them acts fairly freely. However, considering it as a misunderstanding of the experimental method, Skrabal said that the main reaction was



In this case NaOH acted as a catalyst only, and on account of the large quantity

1) H. Staudinger, K. Frey and W. Stark, *Ber.*, 60, 1782 (1927).

2) W. O. Herrmann and W. Haehnel, *Ber.*, 60, 1658 (1927).

3) H. Staudinger and A. Schwalbach, *Ann. Chem.*, 488, 8 (1931).

4) S. Lee and I. Sakurada, *Z. physik. Chem. A* 184, 268 (1939).

Experimental Method and Examinations.

(a) Experimental Method.

About 15 g. of polyvinyl acetate manufactured by the Nippon Chisso Company was dissolved in 500 c.c. of methanol at 20°C., which is here called solution *A*. 10 c.c. of solution *A* was poured into distilled water. The precipitate obtained was filtered, dried, and weighed to know the amount of the polyvinyl acetate used. On the other hand, about 10 g. of sodium hydroxide was dissolved in 400 c.c. of methanol, which is here called solution *B*. The concentrations of both solutions were properly regulated according to the object of the experiment. 80 c.c. of solution *B* was put in a reaction vessel with a stirrer and held in a thermostat kept at $0 \pm 1/10^\circ\text{C}$. 170 c.c. of water and 150 c.c. of methanol being added to it, the mixture was stirred at 0°C. Then, 200 c.c. of solution *A* kept at 0°C. was added to it. The volume change by the mixing being neglected, the ratio of the volumes of water and methanol was found to be $430 : 170 \doteq 2.5 : 1$.

From the reaction system 20 c.c. of the material for analysis was taken out at a time and poured into 500 c.c. of distilled water; some precipitate was then obtained. The polyvinyl acetate thus formed was filtered, washed, dried at 105°C. for 5 hours, and weighed. Thus the progress of saponification reaction was observed from moment to moment.

From the purpose of the rapid coagulation of the precipitate, 5 c.c. of saturated ammonium bicarbonate solution was added. The order of mixing solutions *A* and *B* was determined so as to avoid a temporary turbidity produced immediately after mixing.

By means of Ostwald's viscosimeter placed in the thermostat, viscosity was also measured, using 5 c.c. of the sample which was taken out 5 minutes after mixing. In this case the change of specific gravity could not be measured.

(b) Identification of the Substance Weighed as Polyvinyl Acetate.

By the above stated method, commercial polyvinyl acetate, whose polymerisation degree was 601, was saponified. The precipitate insoluble in water was collected from moment to moment during the reaction and dissolved in methanol till the amount reached a given volume (250 c.c.). 50 c.c. of it was poured into water, and from the precipitate obtained its concentration was estimated, NaOH methanol solution of known concentration was added to the rest of the solution and, from NaOH consumed, the acetyl values as CH_3COOH were calculated, which are shown

in Table I.

It is not strange that the observed values are fairly discrepant from the theoretical value, 69.8%, because the determination of the acetyl value is really hard to make according to the theory. Judging from the fact that the acetyl values are not much different from one another in spite of the progress of the reaction, the substance weighed may be regarded as pure polyvinyl acetate, and not a partially saponified product.

Table I.
Acetyl value of the weighed sample.

Minutes		0	5	10	20	30	40
CH ₃ COOH %	Exp. 1.	63.43	—	—	65.26 (?)	60.53	61.35
	" 2.	61.99	63.33	61.59	—	60.25	61.67
	" 3.	62.32	62.32	60.06	65.26 (?)	62.32	63.32
	" 4.	63.26	60.21	60.53	61.59	60.35	64.32
	" 5.	61.62	63.43	61.59	60.53	64.21	60.06

(c) Identification of the high polymer in the filtrate
a polyvinyl alcohol.

It is important to ascertain whether the high polymer dissolved in water consists of polyvinyl alcohol only, or it contains any partially saponified product. Experiments 1 and 2 were made for this object.

Experiment 1.

The same materials were used as above (b): sodium hydroxide of 3.33 g/L initial concentration and polyvinyl acetate of 10.30 g/L initial concentration. The reaction was made to take place at 0°C. 20, 30, 40, and 50 minutes after the start of the reaction, 500, 300, 200, and 100 c.c. of the solution were collected respectively and poured into distilled water and coagulated quickly with NH₄HCO₃, and then the precipitate (polyvinyl acetate) was separated by filtration. From the mixture of the filtrate and washings, polyvinyl alcohol was easily coagulated, by adding pure Na₂SO₄ of 30 g. per 100 c.c. of the mixture. The coagulated substance was filtered and the precipitate was washed with a saturated solution of sodium sulphate, until it no longer coloured pink with phenolphthalein.

The substance obtained was dissolved in water and made up to 250 c.c.; 50 c.c. of it was poured into acetone and the precipitate (polyvinyl alcohol) was separated and weighed. As this precipitate was very hygroscopic, the weighing

was carried out with the greatest possible care to keep the air out. With the rest of the solution, CH_3COOH was determined by the said method. The analytical values obtained are shown in Table II. From the table, it is clear that the polyvinyl alcohol which is soluble in water has almost perfectly lost the acetyl radical, and that a little amount of CH_3COOH remains adhering owing to imperfect purification or other cause. The analytical values show a tendency of a little decrease as time goes on.

Experiment 2.

The filtrate was evaporated under vacuum and from the solution thus concentrated polyvinyl alcohol was separated with acetone, not by the coagulation method with Na_2SO_4 . The analytical method was the same as before. The result obtained is shown in Table II.

Table II.
Acetyl value as CH_3COOH of the polyvinyl alcohol.

Minutes	30	40	50
Exp. 1.	2.14%	1.27%	0.89%
Exp. 2.	2.03%	1.32%	0.69%

It is clear from this table that the acetyl value of the part of the saponified product, which is soluble in water and coagulated and separated with Na_2SO_4 or acetone, is not greater than 2%, and that it may be regarded as almost pure polyvinyl alcohol in comparison with 69.8%, the theoretical value of polyvinyl acetate.

A very small number of acetyl radicals which decreases according to the lapse of time is considered to depend upon the adsorption of methyl acetate due to the pooriness of the method of purification of such a high polymer.

(d) The Quantitative Correspondence between Polyvinyl Acetate taken and Polyvinyl Alcohol Generated.

By the method mentioned under (a) it was proved that the substance weighed from moment to moment was polyvinyl acetate as examined in (b), and that the other substance soluble in water and separated with either Na_2SO_4 or acetone is almost pure polyvinyl alcohol.

It will be shown now that there is no room for existence of any intermediate high polymer between polyvinyl alcohol and polyvinyl acetate.

Commercial polyvinyl acetate, (mean polymerisation degree=535) was used without fractionation. Saponification reaction was brought about at 0°C . with polyvinyl acetate of 11.300 g/L and sodium hydroxide whose initial concentration was 3.053 g/L. 300 c.c. of the material was collected in aliquots 10, 20, 30, and 40 minutes after the start of the reaction and poured into 700 c.c. of water to which 5 c.c. of the saturated solution of ammonium bicarbonate was added. Over a night it was filtered and washed. The precipitate obtained (polyvinyl acetate) was weighed by the same method as already mentioned. The filtrate was concentrated to about 100 c.c. and poured into 300 c.c. acetone. The following day the precipitate thus obtained was filtered and washed with acetone and weighed according to the method under (c). The quantitative relations of the both are shown in Table III.

The ground molecular weight of polyvinyl alcohol is 44 and that of polyvinyl acetate 86. Though there is such a great difference in the ratio of nearly 1 : 2 between them, the sum of their mols almost agrees with the values obtained irrespective of the lapse of time. It is, therefore, inferred that there is no room for existence of any other substance beside the above two and that the decrease of polyvinyl acetate mol is equal to the increase of polyvinyl alcohol mol.

Table III.

Minutes	0	10	20	30	40
Water insoluble Subs. g/L.	11.3000	8.7696	6.9426	5.5526	0.0360
Mol. as polyvinyl acetate. (above value \div 86)	0.1314	0.1020	0.0807	0.0646	0.0004
Water soluble, acetone insoluble Substance g/L.	0	1.3464	2.2132	2.9832	5.9532
Mol. as polyvinyl alcohol (above value \div 44)	0	0.0306	0.503	0.0678	0.1353
Sum of the both val. mol.	0.1314	0.1326	0.1310	0.1324	0.1357

The Preliminary Examination of the Reaction Velocity.

The above method mentioned under (a) was considered as one of the direct methods of measuring the generated polyvinyl alcohol, and its applicability was proved by the experiments under (b), (c) & (d). The following are preliminary experiments of the saponification of the commercial sample at 0°C . The conditions of the reaction are summarized in Table IV. The progress of the reaction is graphically shown in the following figures, which are very different from those in the ordinary case. It has two remarkable breaks. The concentration of alkali greatly affects the reaction velocity. The polymerisation degree also affects the reaction velocity; the larger the polymerisation degree, the faster the reaction.

The viscosity change of the reaction system was measured; change of the trend of the curve agrees with the said breaks obtained from the above mentioned method of weighing polyvinyl acetate in the reaction system.

The nature of the reaction will be examined in detail in the next report.

Table IV.

No. of Exp.	Mean polym. degree	Initial NaOH conc. g/L	Initial polyvinyl acetate g/mol/L	Minutes for completion of reaction
1	601	3.270	0.1132	45
2	601	3.250	0.1245	55
3	592	3.470	0.1450	45
4	592	3.310	0.1542	55
5	592	2.750	0.1163	120
6	502	3.240	0.1298	80
7	502	3.060	0.1350	115

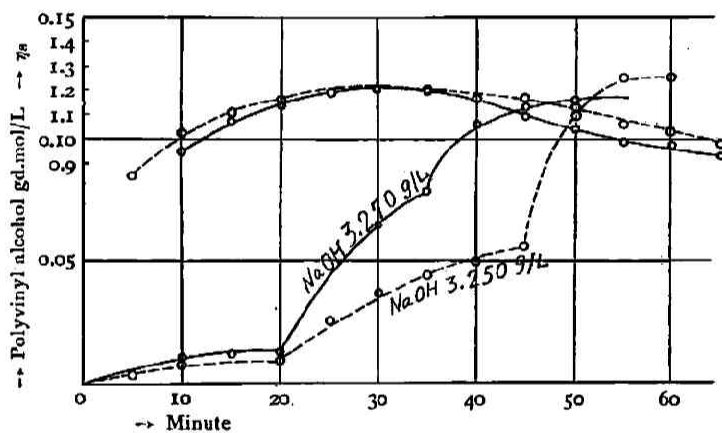


Fig. 1. Exp. 1 and Exp. 2.

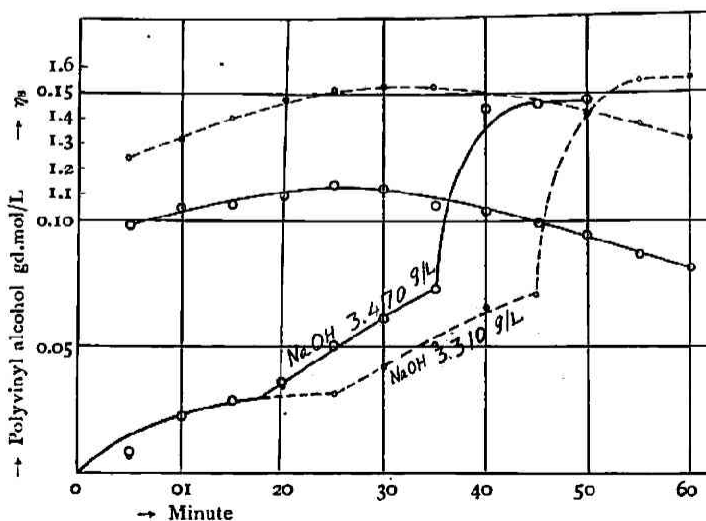


Fig. 2. Exp. 3 and Exp. 4.

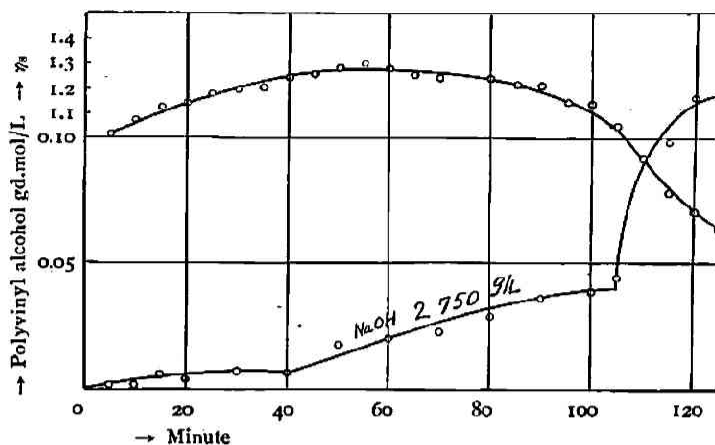


Fig. 3. Exp. 5.

Summary.

The saponification of polyvinyl acetate has been made to take place with alkali in water-methanol solution so as to be treated as a homogeneous reaction in solution. The method of measuring the progress of the saponification by weighing polyvinyl acetate yet unreacted has been adopted. The preliminary experiments were made at 0°C. on commercial polyvinyl acetate. The results obtained are as follows:

(1) When the concentration of polyvinyl acetate yet unreacted is measured during the saponification reaction, the number of the newly formed mols of polyvinyl alcohol is readily given, and there is no room for existence of any partially saponified product. It is, therefore, possible to measure the reaction velocity by this method.

(2) From the preliminary experiments on commercial polyvinyl acetate carried out by the method mentioned in the present report, it has been found that the progress of the reaction is not smooth, but has two remarkable breaks.

(3) The concentration of alkali greatly affects the reaction velocity.

(4) The so-called polymerisation degree affects the reaction velocity; the larger the polymerisation degree, the faster the reaction.

(5) The relation between the progress of the reaction and the viscosity change has been investigated. The viscosity change is also represented by a curve with breaks corresponding to the curve obtained by the weighing method.

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